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(21) International Application Number: PCT/GB97/01522 (22) International Filing Date: 6 June 1997 (06.06.97) (30) Priority Data: 12 June 1996 (12.06.96) GB (71) Applicant (for all designated States except US): HORSELL GRAPHIC INDUSTRIES LIMITED [GB/GB]; Howley Park Estate, Morley, Leeds LS27 0QT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BENNETT, Peter, An- drew, Reath [GB/GB]; 15 Apley Close, Harrogate, N. Yorks HG2 8PS (GB). SMITH, Carole-Anne [GB/GB]; 26 Paw- son Street, Morley, Leeds LS27 0QA (GB). BAYES, Stuart [GB/GB]; 10 Chatsworth Mews, Morley, Leeds LS27 8AB (GB). RILEY, David, Stephen [GB/GB]; 8 Reedsdale Drive, Gildersome, Leeds LS27 7JG (GB). (74) Agent: MATTHEWS, Richard, Nordon; Ilford Ltd., Town Lane, Mobberley, Knutsford, Cheshire WA16 7JL (GB).		(81) Designated States: AU, CA, CN, CZ, GB, IL, JP, KR, NO, NZ, PL, RU, US, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: LITHOGRAPHIC PLATES (57) Abstract <p>There is described a method of preparing a printing form which comprises coating on a lithographic support having a hydrophilic surface, a layer of a radiation sensitive ink, imaging the ink coating by digital means, then acting on the plate with aqueous dampening rollers to remove the unexposed areas of the ink coating to reveal the hydrophilic surface of the plate and to leave an ink image formed from the ink, which is oleophilic after exposure.</p>		

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LITHOGRAPHIC PLATES

This invention relates to a digital printing method and especially to a method for preparing an imaged lithographic plate on-or-off press using a digitally controlled laser output.

- 5 Currently the commonest method of preparing a lithographic plate is to image a photosensitive lithographic plate using an image mask, such as a photographic negative, and to prepare the plate therefrom using an aqueous developing solution. This procedure is time consuming and requires facilities and equipment to support the necessary chemistry.
- 10 Thus recently, various methods have been proposed for preparing lithographic plates on the press which is to be used to produce prints from the plate. These methods prepare the image using a digitally controlled laser image head. As described in E.P.A. 580393 such methods include ink-jet methods digitally controlled, spark-discharge methods and the production of
- 15 electromagnetic-radiation pulses that create chemical changes of the plate blank. Also etching methods have been described as well as blank plates which are ablated by the laser to form an ink-receptive image.

We have discovered a novel method of preparing a printing form using a digitally controlled laser output from an imaging head which may be

20 employed on-or-off a press.

According to the present invention there is provided a method of preparing a printing form which comprises coating on a lithographic support having a hydrophilic surface a layer of a radiation sensitive ink, imaging the ink coating by digital laser means, then acting on the plate with aqueous dampening

25 rollers to remove the unexposed areas of the ink coating to reveal the

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hydrophilic surface of the support and to leave an ink image formed from the ink, which is oleophilic after exposure.

The support is a material suitable for use on lithographic presses and may be metal, plastic or paper. Typical metals are aluminium, chromium or steel.
5 Typical plastics are polyethylene terephthalate or polycarbonate.

The surface of the lithographic support is suitably treated to render it hydrophilic and adherent for the ink. Thus it may be anodised aluminium, chromium or it may be of a plastics material which is either hydrophilic or which has been treated to render it hydrophilic, for example polyethylene
10 terephthalate coated with hydrophilic layers as described in our PCT Application GB96 02883 and WO94/18005 (Agfa).

Most preferably the support is metal and this is in the form of a sleeve or cylinder which fits on to a printing press. Most preferably the method of the present invention is carried out in situ in a printing press. Thus the printing
15 press comprises an ink train which when the metal sleeve is mounted on the press can be lowered to coat on the sleeve an ink coating of a required thickness, together with a digital laser imaging head, means to disengage the metal sleeve from the printing press and to rotate it at a speed suitable for imaging, and water dampening rollers.

20 A preferred method for the use of flexible lithographic supports is to have a roll of the hydrophilic support within the press which when new material is required dispenses the new substrate and recoils the used substrate automatically. Such a system is utilised commercially in the Heidelberg Quickmaster DI press and on-press imaging system. In such a system all
25 operations are carried out in-situ on the press with the exception of occasional renewal of the roll of hydrophilic support material.

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Means are present in the ink-train to coat any required thickness of ink on the metal sleeve. For example for a lower run length an ink thickness of 0.1 to 0.5 microns is suitable. But for a higher run length a thickness of 3 microns is suitable.

- 5 The digital laser imaging head is in essence an image setter attached to the printing press and comprises a laser which scans in an imagewise manner radiation across the plate in response to image signals stored in a computer.

The laser may emit in the U.V waveband, as white light or preferably in the infra-red region of the spectrum.

- 10 Preferably the radiation sensitive ink comprises a radiation absorbing material which allows the ink to be sensitive to the wavelength of the radiation emitted by the image scanning means.

Conveniently the scanning means is a laser beam having a wavelength of above 600nm. Usefully the radiation sensitive ink comprises an infra-red
15 absorbing compound. Suitable infra-red absorbing compounds include pigments such as phthalocyanine pigments or dyes of the following classes. squarylium, cyanine, merocyanine, indolizine, pyrylinium or metal dithiolene dye.

Preferably the infra-red absorbing compound is one whose absorption
20 spectrum is significant at the wavelength output of the laser which is to be used in the method of the present invention. For example gallium arsenide diode lasers emit at 830nm and Nd YAG lasers emit at 1064nm.

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Carbon black is also a useful radiation absorbing compound and in the context of this invention it can also be used as the colourant for the black radiation sensitive ink.

Preferably the radiation sensitive ink comprises a radiation sensitive resin 5 which hardens or cross-links when irradiated. Suitable radiation sensitive resins are certain acrylate resins, for example polyether acrylate, epoxy acrylate, and alkyl acrylate. Suitable solvents for example styrene or methyl acrylate may also be present as well as a photopolymerisation initiator such as benzophenone or p-dialkyl-aminobenzoic acid.

10 Preferably the dampening rollers are covered with a lithographic fountain solution.

Thus in the preferred method of the present invention a metal sleeve or cylinder which has a hydrophilic surface and which forms part of the printing surface of a printing press is coated with a predetermined thickness of a 15 radiation sensitive ink. the metal sleeve is disengaged from the roller drive of the printing press and is caused to rotate at a speed suitable for imaging. the digital laser head attached to the printing press images the ink layer on the metal sleeve. after imaging the metal sleeve is re-engaged to the roller drive of the printing press and the rollers of the press rotate and act as 20 water-dampening rollers. thus removing the unexposed areas of the ink on the surface of the sleeve and to reveal the hydrophilic surface of the sleeve in the unexposed areas of the sleeve. the rollers of the press are then inked up and the printing press prints on to paper fed to it. After the print run has finished a plate washer can be employed to remove all the ink from the sleeve which can 25 then be re-used.

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Preferably the metal sleeve can be removed from the press to clean it thoroughly and also to renew it periodically.

Preferably details of the required film thickness to be coated on the sleeve are fed directly into the laser imaging head which is programmed to adjust incident power and scanning speed to provide the optimum cure and imaging resolution.

Conveniently the same radiation sensitive ink is used to form the initial coating on the metal sleeve and in the actual print run. Thus ensures that the ink used in the print run will have a high affinity for the image areas.

10 Some advantages of the proposed method of the present invention are that only the film thickness necessary to do the job need be employed which in turn means recording time is minimised. This means for this system that make ready time is directly proportional to run length which is exactly what is required for a Direct-to-Press system. i.e. make ready time reduces as run
15 length reduces in cases where imaging power is constant.

The digital inking controls can be arranged to communicate with the digital head allowing feedback loops to ensure maximum added value in terms of make-ready.

The idea of a removable sleeve is beneficial in case the surface becomes
20 scratched and a spare can be used. It may also be possible to have them conditioned on a maintenance basis for optimum hydrophilicity.

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Testing sensitivity of coatings

The coated substrate to be imaged was cut into a circle of 105mm diameter and placed on a disc that could be rotated at constant speed at between 100 and 2500 revolutions per minute. Adjacent to the spinning disc a translating table held the source of the laser beam so that the laser beam impinged normal to the coated substrate. while the translating table moved the laser beam radially in a linear fashion with respect to the spinning disc.

The laser used was a single mode 830nm wavelength 200mW laser diode which was focused to a 10 micron resolution. The laser power supply was a 10 stabilised constant current source.

The exposed image was in the form of a spiral whereby the image in the centre of the spiral represented slower scanning speed and long exposure time and the outer edge of the spiral represented fast scanning speed and short exposure time. Imaging energies were derived from the measurement of the 15 diameter at which the image was formed.

The diameter of the spiral can be equated to mJ/cm^2 in terms of pixel energy density. The minimum energy that can be delivered by this exposure system is 150mJ cm^2 at an rpm of 2500. These sensitivities are quoted in the Examples 20 which follow: the higher the figure the less the sensitivity.

In the Examples commercially available black inks all containing carbon black were used.

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EXAMPLE 1 Heat Set Ink

Gibbons Heat Set Black Ink (Gibbons Inks and Coatings Limited) was coated onto discs of grained and anodised aluminium using a rubber inking roller to give a wet ink film weight of 7.0 to 9.0 g/m².

5 The coated disc was imaged with a 200mW, 830nm. near infrared laser source at various speeds to give a range of energy densities incident on the coating's surface.

The disc was then developed by application of a 2% solution of Emerald fountain solution (Anchor Pressroom Chemicals) in water and rubbing this
10 with cotton wool to remove the unexposed ink coating leaving behind the exposed coating areas.

The typical sensitivity obtained with this system was 1850 mJ/cm² pixel energy density.

EXAMPLE 2 Metal UV Cure Ink

15 Example 1 was repeated using Eurocure MD UV SPX190 Black ink (Edward Marsden Inks) to give wet ink coating weights from 2.5 to 6.5 g/m² and a typical sensitivity of 4900 mJ/cm² in terms of pixel energy density.

EXAMPLE 3 UV Cure Ink

Example 1 was repeated using Coates UV Cure Black Ink (Coates-Lorillaux)
20 to give wet ink coating weights from 4 to 7g/m² and a typical sensitivity of 2700 mJ/cm² pixel energy density.

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EXAMPLE 4 Metal Heat Set Ink

Example 1 was repeated using Diaflex Van Dyke Black TP Ink (Heat set type, Edward Marsden Inks) to give wet ink coating weights of 4 to 5.5 g/m² and a typical sensitivity of 1850 mJ/cm² pixel energy density.

5 EXAMPLE 5 Heat Set Ink On Silicated Substrate

Example 1 was repeated on a grained, anodised and silicated aluminium substrate.

The typical coating weight was 7 to 9 g/m² and the sensitivity seen was 1850 mJ/cm².

10 Method For Production Of Silicated Substrate

Grained and anodised aluminium substrate with a phosphate post anodic treatment was immersed for 30 seconds in an aqueous, 3% solution of sodium silicate heated to 50°C. On removal the substrate was washed under cold tap water and finally dried for 5 minutes at 80°C.

15 EXAMPLE 6 Heat Set Ink With Added Infrared Dye KF646 PINA

Example 1 was repeated except an infrared absorbing dye: Sensitiser KF646 PINA (Riedel de Haen AG), was added to the ink to increase its infrared sensitivity.

Formulation: 0.3g of thermal set black ink

20 0.18g of 3.2% Sensitiser KF646 in methoxy propanol.

This formulation was mixed with a palette knife and then applied to discs of substrate, imaged and developed as in previous examples.

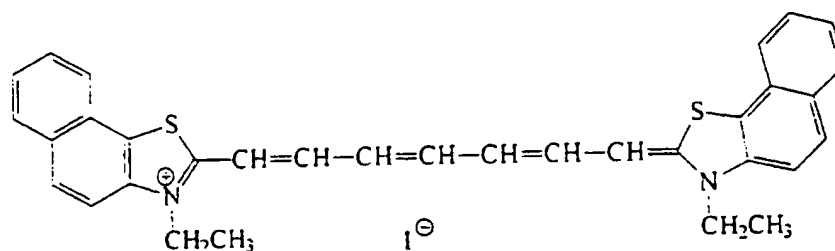
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Typical wet ink coating weights were from 3 to 10 g/m², giving a sensitivity of 1700 mJ/cm² when optimised.

EXAMPLE 7 Heat Set Ink With Added Infrared Dye NK 1887

Example 6 was repeated except the infrared absorbing dye used was NK 1887 (supplied by Nippon Kankoh-Shikiso Kenkyusho) at 3.2% w/w in dimethylformamide.

Dye NK1887 is:-



3-Ethyl-2-{7(3-ethyl-naphtho[2.1-d]-thiazolinylidene)-1.3.5-heptatrienyl}naphtho[2.1-d]-thiazolium iodide.

10 Typical coating weights applied were from 2.5 to 5 g/m² giving a sensitivity of 1350 mJ/cm², when optimised.

EXAMPLE 8 UV Ink with Added Infrared Dye KF646 PINA

The Coates UV cure black ink was mixed with Sensitiser KF646 PINA as in the below formulation:

- 15 0.3g Coates IV cure black ink.
 0.18g of KF646 PINA at 3.2% in methoxy propanol.

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The formulation was blended using a palette knife and applied to substrate discs with a rubber inking roller, then imaged and developed as in previous examples.

Coating weights of 2 to 5 g/m² were obtained giving an optimised sensitivity of 1100 mJ/cm².

EXAMPLE 9 UV Cure Ink With Added Infrared Dye NK1887

Example 8 was repeated substituting the NK 1887 infrared dye for the KF646 PINA.

Wet coating weights of 2 to 4 g/m² were obtained, giving a sensitivity of 1500 mJ/cm² pixel energy density.

EXAMPLE 10 Heat Set Ink With Sensitiser KF646 On Silicated Substrate

Example 6 was repeated on silicated substrate.

Typical wet coating weights of 3 to 5.5 g/m² were examined giving a sensitivity of 1100 mJ/cm².

15 EXAMPLE 11 Heat Set Ink with NK1887 Infrared Dye on Silicated Substrate

Example 7 was repeated on silicated substrate, giving wet coating weights of 2.5 to 5g/m² and sensitivities around 1370 mJ/cm² pixel energy density.

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EXAMPLE 12 UV Ink with Sensitiser KF646 PNA on Silicated Substrate

Example 8 was repeated on silicated substrate.

Wet ink coating weights of 3 to 5g/m² were found to give sensitivities around 1360 mJ/cm² when optimised.

5 EXAMPLE 13 UV Cure Ink With Acid Generator (Triazine)

The acid generating triazine 2(4-phenylthiomethyl)-4,5-trichloromethyl-s-triazine was mixed at 3% by weight with U.V. cure ink as follows:

0.4g Coates UV Cure Black Ink

0.3g triazine at 4% w/w in methyl ethyl ketone

10 The mixture was blended with a palette knife and applied to substrate discs then imaged and developed as in previous examples.

Coating weights of 2.5 to 4 g/m² were obtained and sensitivities of around 1300mJ/cm² obtained.

In the Examples above, dye KF646 was supplied by Riedel de Haen. It is a
15 benzthiazole based heptamethine cyanine dye. λ_{max} 792nm in MeOH.

EXAMPLE 14

Example 6 was repeated using a reduced coating weight on a silicated support. the coated plate was imaged in a horizontal bed image setter as described below.

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A form to be imaged was cut into a sample of 262 by 459mm and placed on a flat metallic bed. Suspended above the sample was a laser scanning system which directed a focused laser beam over the sample surface by means of XY scanning mirror (two galvanometer scanning mirrors in orthogonal planes). The included scan angle of this system was 40° capable of scanning up to 7 rad s^{-1} (or 850 mm s^{-1} at the focal plane). The image to be exposed could be chosen from any image capable of being converted into vector co-ordinates via a CAD package, this including images raster scanned onto the sample surface. The scan speed and dwell time of the laser were selectable by the operator using the scanner's control software in order to obtain various imaging energy densities.

The laser diode used was a single mode 830nm wavelength 200mW laser diode which was collimated and then focused, after reflection by the XY scanning mirrors, to do a 10 micron spot at the $1/e^2$ points. The laser power supply was a stabilised constant current source.

The coating weights of from 1.2 to 2.1 g/m^2 were tested giving a sensitivity of around 450 mJ/cm^2 .

EXAMPLE 15.

The acid generating triazine 2(4-phenylthiomethyl)-4,5-trichloromethyl-s-triazine was mixed at 3% weight to weight with U.V cure ink as follows:

0.4g Coates UV Cure Black Ink

0.3g triazine at 4% w/w in methyl ethyl ketone

The mixture was blended with a palette knife and applied to substrate then imaged on the horizontal bed image setter as described above.

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Coating weights of 1.3 to 1.7 g/m² were used and sensitivities of around 700mJ/cm² obtained.

EXAMPLE 16.

0.3g of Gibbons Heat Set Black Ink (Gibbons Inks and Coatings Limited) was
5 mixed with 0.18g of 3.2% w/w NK 1887 (supplied by Nippon
Kankoh-Shikiso Kenkyusho) in dimethylformamide using a palette knife. The
mixture was coated onto grained and anodised aluminium using a rubber
inking roller to give a wet ink film weight of 1.2 to 2.0g/m². The coated plate
was imaged on the horizontal bed image setter as described above. The plate
10 was then developed by application of a 2% solution of Emerald fountain
solution (Anchor Pressroom Chemicals) in water and rubbing this with cotton
wool to remove the unexposed ink coating leaving behind the exposed coating
areas. The typical sensitivity obtained with this system was 750mJ/cm².

After development, the plate was mounted on a Heidelberg Speedmaster 52
15 printing press and printed copies produced. During this runlength test, at least
10,000 copies were obtained from this plate.

Even though some of the above listed inks are stated to be U.V. sensitive they
are all infra-red sensitive as they contain carbon black.

It is to be understood that it is not necessary to coat the plate for the printing
20 step with the same ink as used in the imaging step. Any other black or other
coloured ink can be used.

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Claims:-

1. A method of preparing a printing form which comprises coating on a lithographic support having a hydrophilic surface a layer of a radiation sensitive ink. imaging the ink coating by digital laser means. then
5 acting on the support with aqueous covered dampening rollers to remove the unexposed areas of the ink coating to reveal the hydrophilic surface of the support and to leave an image formed from the ink. which is oleophilic after exposure.
2. A method according to claim 1 wherein the dampening rollers are
10 covered with lithographic fountain solution.
3. A method according to claim 1 wherein the surface of the lithographic support is anodised aluminium. chromium or suitable treated plastics material.
- 15 4. A method according to claim 1 wherein the lithographic support is a sleeve or cylinder which fits on to a printing press.
5. A method according to claim 1 wherein the method as claimed is carried out in situ in a printing press.
6. A method according to claim 1 wherein the laser emits radiation above
20 600 nm.
7. A method according to claim 1 wherein the ink is sensitive to infra-red radiation. UV radiation or visible light.

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8. A method according to claim 7 wherein the ink comprises a radiation absorbing material.
9. A method according to claim 8 wherein the radiation absorbing compound absorbs radiation above 600 nm.
- 5 10. A method according to claim 9 where the radiation absorbing compound is selected from a dye or pigment.
11. A method according to claim 10 wherein the pigment is a phthalocyanine pigment.
12. A method according to claim 10 wherein the dye is selected from one
10 of the following classes. squarylium, merocyanine, cyanine, indolizine, pyrylium or metal dithioline.
13. A method according to claim 8 wherein the ink comprises carbon black as a radiation absorbing material.
14. A method according to claim 13 wherein the ink also comprises an
15 infra-red absorbing dye.
15. A method according to claim 1 wherein the ink comprises a radiation sensitive resin.
16. A method according to claim 15 wherein the radiation sensitive resin hardens or crosslinks on exposure to radiation.
- 20 17. A method according to claim 16 wherein the resin is selected from acrylate resins.

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18. A method according to claim 16 wherein the ink comprises a polymerisation initiator.
19. A method according to claim 18 wherein the polymerisation initiator is photolytically decomposed on exposure to suitable radiation.
- 5 20. A method according to claim 18 wherein the radiation initiator is thermally decomposed on exposure to suitable radiation.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/01522

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41C1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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PCT/GB 97/01522

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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